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(21) International Application Number: PCT/NL96/00218 (22) International Filing Date: 3 June 1996 (03.06.96) (30) Priority Data: 1000495 2 June 1995 (02.06.95) NL (71) Applicant (for all designated States except US): COÖPERATIEVE VERKOOP- EN PRODUCTIEV- ERENIGING VAN AARDAPPELMEEL EN DERIVATEN AVEBE B.A. [NL/NL]; Beneden Oosterdiep 27, NL-9641 JA Veendam (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): HEERES, Andre [NL/NL]; Taco Mesdagstraat 23a, NL-9718 KJ Groningen (NL). BLEEKER, Ido, Pieter [NL/NL]; Poldermolen 22, NL-9791 LS Ten Boer (NL). GOTLIEB, Kornelis, Fester [NL/NL]; Wildervanckstraat 12, NL-9643 LC Veendam (NL). VAN DOREN, Hendrick, Arend [NL/NL]; Hanck- emaborg 5, NL-9722 WD Groningen (NL). (74) Agent: SMULDERS, Th., A., H., J.; Vereenigde Octrooibu- reaux, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: OXIDIZED POLYMERIC CARBOHYDRATE ETHERS FOR USE AS SEQUESTERING AGENT, AND METHODS FOR THE PREPARATION THEREOF		
(57) Abstract The invention relates to oxidized polymeric carbohydrate ethers or mixtures thereof with a degree of polymerization of at least 10. These compounds possess an excellent sequestering and anticrustation activity and are therefore used with advantage in cleaning agents. The invention further relates to a method for the preparation of oxidized carbohydrate ethers, wherein at least a part of the primary hydroxyl groups of polymeric carbohydrate ethers with a degree of polymerization of at least 10 are selectively oxidized.		

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Title: Oxidized polymeric carbohydrate ethers for use as sequestering agent, and methods for the preparation thereof.

The invention relates to oxidized carbohydrate derivatives, more particularly oxidized carbohydrate ethers, or mixtures thereof. The invention further relates to the use of these carbohydrate ethers as sequestering agent and/or anticrustation agent, as well as to methods for the preparation thereof. The products according to the invention have eminent properties regarding the complexing of metal ions, in particular calcium. These properties can be used advantageously, for instance in detergent formulations.

Modern detergents and, more generally, cleaning agents, consist, both in solid and liquid form, of complex mixtures of compounds, such as surfactants, bleaching agents, bleach activators, enzymes, fabric softeners, odorants and the like. In addition, these products conventionally comprise an ingredient specifically intended to bind the metal ions, and in particular calcium and magnesium ions, present in mains water, by complexing. This complexing should occur in such a manner that the metal ions present do not adversely affect the activity of the other detergent ingredients and that the complex does not precipitate on the materials to be washed and remains behind (anticrustation).

Until the mid-'80s, phosphates, in particular sodium tripolyphosphate, were used for this metal ion binding activity. On account of their eutrophying activity, phosphates in detergents have since been forbidden by law in many countries.

Presenting as substitutes were zeolites and/or polycarboxylic acids/carboxylates, such as nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), citric acid and polymeric polycarboxylates, for instance polymers with acrylate, maleate or methacrylate groups. These so-called phosphate substitutes, however, also have several disadvantages, for instance a relatively small extent of

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biodegradability. Moreover, they are generally prepared from petrochemical raw materials, the availability of which will diminish in the future. Therefore, in the past decades a great deal of research has been conducted on the preparation, 5 characterization and application possibilities of polycarboxylates based on natural raw materials, in particular carbohydrates and derivatives derived therefrom.

The preparation of oxidation products of low-molecular carbohydrates and derivatives derived therefrom and of high- 10 molecular carbohydrates, which oxidation products comprise polycarboxylates in particular, has been described extensively in the literature.

Carbohydrate-containing polycarboxylates can be prepared, for instance, by reacting carbohydrates with compounds that 15 contain carboxyl groups. Thus a carboxymethyl derivative can be obtained by allowing the carbohydrates to react with monochloroacetic acid. Activated acrylic acid derivatives are also widely employed. The products obtained have various possibilities for application, inter alia as cation exchanger 20 (see e.g. Chemical Abstracts, 109: 8322w), as an ingredient of granular fertilizer (Chemical Abstracts, 78: 57049n), as a dispersing and liquefying agent for ceramic clay (DE-A1-42 43 703), as support material, stabilizer and solubility increasing agent (WO 91/04988) and as immunologically active 25 compounds (Y. Ohya et al., Carbohydr. Polym., 25 (1994) 123-130).

In Japanese patent publication 51-017387 printing ink thickeners are described. These viscosity increasing agents are obtained by oxidizing carboxymethyl cellulose in an 30 alcohol/water (80:20) mixture with hypochlorite at a temperature of 60°C and at a pH of 2.5. This oxidation reaction is not selective, for which reason cellulose is first etherified to carboxymethyl cellulose to protect the secondary OH groups.

35 This oxidation reaction cannot be applied to starches. Under the vigorous conditions under which the reaction is carried out, starch hydrolyzes.

It is noted that the viscosity of the oxidized carboxymethyl cellulose product is not lower than before the oxidation reaction. This points to a low efficiency, which can be accounted for by the presence of alcohol which can also be oxidized under the reaction conditions outlined. By far the most important area of application, however, is the use as sequestering agent, in particular in cleaning agents, such as detergents.

The preparation of carbohydrate-containing polycarboxylates for use in detergents has been described *inter alia* in the following publications: GB-A-1,412,524 (preparation of carboxymethyl derivatives of starch); DE-A1-39 28 310, corresponding to US-A-5,223,642 (etherification of low-molecular carbohydrates with ethylene oxide, followed by oxidation to polycarboxylic acids); WO 93/16110 and DE-A1-42 03 923 (oxidation of polysaccharides by means of $\text{NO}_2/\text{N}_2\text{O}_4$ in the presence of oxygen); DE-A1-42 28 786 (use of oxidized carbohydrates in washing-up compositions); DE-A1-35 35 720 (preparation of tricarboxysucrose); and EP-A1-0 542 496 (preparation and use of C(6)/C(2)-C(3) oxidized starch). These publications contain a great many references to older literature in the field of the preparation and use of oxidized carbohydrates.

Other, more recent, publications in the field of preparation, use and biodegradability of oxidized carbohydrates are, for instance S. Matsumura et al., J. Am. Oil Chem. Soc., 71 (1994) 749-755 (partially dicarboxylated amylopectin); E. Santacesaria et al., Carbohydr. Polym., 23 (1994) 35-46 (oxidized malto-oligomers); Y. Ohya et al., Carbohydr. Polym., 25 (1994) 123-130 (dicarboxyglucomannan); A.C. Besemer et al., Starch/Stärke, 46 (1994) 101-106 (dicarboxyamylodextrins and dicarboxyinulin); and S. Matsumura et al., Polym. Degrad. Stabil., 45 (1994) 233-239 (dicarboxy starch and dicarboxyxylan).

The oxidation of carbohydrates to polycarboxyl compounds can be carried out with a great variety of reagents. Mentioned here by way of example are (air) oxygen, hydrogen peroxide,

sodium hypochlorite or sodium hypobromite, periodic acid or metaperiodate, lead(IV) acetate, $\text{NO}_2/\text{N}_2\text{O}_4$ and cerium(IV) salts. Electrochemical methods have also been described.

It is known that a number of the above-mentioned reagents
5 react with primary hydroxyl groups and oxidize them to carboxyl groups. Primary hydroxyl groups in carbohydrates are mostly attached to the C(6)-atom of each monosaccharide fragment, inter alia in starch and cellulose.

Other reagents effect a so-called diol cleavage. In the
10 case of cellulose and starch, inter alia, in this diol cleavage, the carbon-carbon bond between C(2)- and C(3)-atoms is broken. Initially, dialdehyde starch and dialdehyde cellulose, respectively, are obtained, which are thereafter further oxidized to dicarboxy starch and dicarboxy cellulose,
15 respectively.

In addition, methods have been described where both (partial) diol cleavage and (partial) oxidation of primary hydroxyl groups occur. A number of the above-mentioned reagents also give rise to a partial degradation of the
20 polymeric chain of the oxidized carbohydrates.

An example of such a non-selective oxidation method is given in British patent specification 1,299,646. In this patent specification, a method is described in which an aqueous starch slurry is hydrolyzed to a DE value of 5-70%,
25 whereafter the hydrolysate is oxidized to aldonic acids. In the oxidation step, glucose units present in the hydrolysate, that is, the aldehyde group-containing units, are converted to aldonic acid. Then the obtained aldonic acid group-containing product can be carboxymethylated in order to introduce more
30 complexing capacity. To that end, monochloroacetic acid is added, which agent introduces carboxyl groups non-selectively.

During the process described in this British patent specification, breakdown of the polymeric chain occurs, which is undesired, at least for the method and products according
35 to the present invention.

In general, it can be stated that carbohydrates in which specifically oxidation at the C(6)-atom has occurred, have a

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sequestering activity, which activity, however, is not very great. By contrast, compounds which have been obtained after diol cleavage generally have a good sequestering activity, at least, given a sufficiently high carboxyl content.

- 5 Unfortunately, the biodegradability decreases markedly with an increasing carboxyl content. A high percentage of intact (gluco)pyranosations, by contrast, is favorable with regard to biodegradability.

There is a need for compounds in which a good
10 sequestering activity is accompanied by a reasonable to good biodegradability. To that end, a high carboxyl content and a high content of intact pyranose units is combined.

A.E.J. de Nooy et al. described in an article in
Recl. Trav. Chim. Pays-Bas, 113 (1994) 165-166 the selective
15 oxidation of primary hydroxyl groups of soluble starch and inulin with an oxidizing sodium hypochlorite/bromite system in the presence of 2,2,6,6-tetramethyl-1-piperidyl-N-oxyl (TEMPO) as catalyst.

International patent application 95/07303 describes a
20 method for oxidizing carbohydrates with a primary hydroxyl group, such as starch, cellulose and inulin, as well as fractions and derivatives thereof not further specified or illustrated, by treatment with hypohalogenite in the presence of a catalytic amount of TEMPO in a water-containing medium at
25 a pH of 9-13. In this method, products are formed which have a high content of carboxyl groups without the occurrence of substantial chain degradation.

According to the present invention, it has now been found that when carbohydrate derivatives, and particularly
30 carbohydrate ethers, are oxidized, products are obtained which possess a markedly improved sequestering activity.

Accordingly, the invention relates to oxidized polymeric carbohydrate ethers or mixtures thereof with an average degree of polymerization of at least 10. The term 'degree of
35 polymerization' is intended to refer to the number of monosaccharide units of which the polymeric molecules are made up.

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As will be explained in detail in the examples below, the influence of the extent of oxidation on the sequestering capacity is considerable. The sequestering capacity increases as a function of an increasing carboxyl content. This increase
5 does not proceed linearly; upon further oxidation, the sequestering capacity increases to a greater extent than might be expected on the ground of the increase of the carboxyl content. For known polycarboxyl compounds, explanations for this behavior have been proposed in the literature (see inter
10 alia M.S. Nieuwenhuizen et al., J. Am. Oil Chem. Soc., 60 (1983) 120-124). Generally speaking, it has been found that the presence of multidentate conformations, in which both carboxyl groups and oxygen atoms of ether compounds contribute, in the polycarboxyl compounds is highly favorable
15 with regard to the sequestering activity. The formation of such favorable conformations does not proceed linearly with the increase of the carboxyl content. Accordingly, with a view to as high a sequestering activity as possible, it is preferred to have the oxidation proceed as completely as
20 possible.

For an optimum combination of desired properties and in particular of the biodegradability and the sequestering capacity, however, a lower degree of oxidation can be advantageous. All this can be experimentally optimized by
25 those skilled in the art, depending on factors such as the amount of reagents, reaction time, the carbohydrate derivative used, and the desired application.

Preferably, the polymeric carbohydrate ethers are oxidized to such an extent that multidentate conformations can
30 form when these ethers are brought into a solution.

The oxidized polymeric carbohydrate ethers according to the present invention possess an improved activity compared with oxidized polymeric carbohydrates such as polyglucuronic acid when they possess a carboxyl content of at least 5 milli-
35 equivalents per gram. The sequestering capacity expressed as the reciprocal of the amount of sample (in grams) necessary to

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reduce the calcium ion concentration of a 200 ml solution from 10^{-1} to 10^{-5} mol/l is then at least 2 g⁻¹.

With a view to as high a sequestering activity as possible, a highest possible carboxyl content is preferred.

- 5 The maximum carboxyl content to be achieved, for that matter, is dependent *inter alia* on the type of substituent and the degree of substitution DS.

The products according to the invention have a number of advantages compared with the known oxidized compounds based on carbohydrates, for instance because they have each of the following properties:

- a high carboxyl content, which moreover can be varied as desired;
- excellent sequestering capacity;
- 15 - good stability in a wide pH range;
- composed substantially entirely of intact monosaccharide units, which promotes biodegradability.

Moreover, during the preparation of the products according to the invention, no or substantially no breakdown of the carbohydrate chain occurs.

The oxidized polymeric carbohydrate ethers are obtainable by (selective) oxidation of at least a part, and optionally all, of the primary hydroxyl groups in polymeric carbohydrate derivatives with a degree of polymerization of at least 10.

- 25 For instance, the carbohydrate ethers can be obtained in that first the primary hydroxyl groups in a non-substituted polymer are oxidized and then are etherified. If desired, thereafter again an oxidation reaction can be carried out in order to convert primary hydroxyl groups in the substituents which have been introduced into the polymeric carbohydrate via an ether bond, to carboxyl groups.

- As starting material for the oxidized carbohydrate ethers according to the invention can serve, for instance, substituted or unsubstituted carbohydrate ethers or other polymeric carbohydrate derivatives which contain primary hydroxyl groups. Suitable starting materials are starch
- 35

derivatives such as carboxymethyl starch, hydroxyethyl starch, hydroxypropyl starch, dihydroxypropyl starch, C₁₋₈ alkyl starch, cyanoethyl starch and nitro-C₁₋₈ alkyl starch; cellulose derivatives, such as carboxymethyl cellulose, 5 hydroxyethyl cellulose, hydroxypropyl cellulose, dihydroxypropyl cellulose, C₁₋₈-alkyl cellulose and cyanoethyl cellulose; and derivatives of other polysaccharides, provided they contain primary hydroxyl groups. Preferably used as starting material for the oxidation reaction are hydroxyethyl 10 starch and, in particular, carboxymethyl starch.

In this description and in the claims, the term "starch" comprises starch from random sources, such as potatoes, wheat, maize, tapioca, peas, rice and millet; as well as genetically modified variants thereof. The starch can consist of amylose 15 and/or amylopectin; amylose and amylopectin can occur in all kinds of relative ratios. Further, the starch can be partially decomposed chemically or enzymatically or treated otherwise, for instance cross-linked, before starch ethers are prepared therefrom. The term starch also comprises debranched starch. 20 Debranched starch consists for the most part of relatively short α (1-4)-bound glucose chains having an average degree of polymerization of about 15-25.

If desired, also mixtures of carbohydrate ethers can be used as starting material for the oxidation reaction and/or 25 the oxidized carbohydrate ethers can be mixed prior to their intended use.

The carbohydrate ethers which serve as starting material for the preparation of the products according to the invention can be prepared by conventional methods. The amount of ether 30 substituents expressed as degree of substitution (DS) and represented in moles per mole anhydromonosaccharide units in the polysaccharide, or as molar substitution (MS), likewise represented in moles per mole anhydromonosaccharide units, can vary from 0 to 2 or higher, preferably from about 0.5 to 1.5, 35 and in particular about 1.

The invention also relates to a method for the preparation of oxidized carbohydrate ethers, in which at least

a part of the primary hydroxyl groups of polymeric carbohydrate ethers with a degree of polymerization of at least 10 is selectively oxidized. In principle, this oxidation reaction can be carried out with all reagents that oxidize
5 primary hydroxyl groups with a certain degree of specificity.

Preferably, the reaction is carried out using a catalytic amount of stable nitroxide radicals in the presence of a suitable oxygen donor as oxidizing agent. In particular, TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) is preferred as
10 catalyst. With this catalyst, as is known from the above-mentioned international patent application 95/07303 and the article of De Nooy et al, primary hydroxyl groups can be oxidized highly selectively. Additionally, it has been found by the present inventors that this catalyst can be recovered
15 from the reaction mixture in a simple manner and be re-used in a next reaction cycle (see Dutch patent application 1000396).

Sodium hypochlorite, optionally in combination with sodium bromide, from which combination hypobromite is formed in situ, is preferably used as oxygen donor.

20 The invention accordingly comprises the selective oxidation of primary hydroxyl groups in carbohydrate derivatives to carboxyl groups, using stable nitroxide radicals and sodium hypochlorite/bromite. This reaction can be carried out in a very simple manner, under mild conditions and
25 on a large scale, in an aqueous solution or suspension, while after the reaction the catalyst can be recovered from the reaction mixture in a simple manner.

In a typical embodiment, a carbohydrate derivative, preferably a carbohydrate ether, is dissolved or suspended in
30 water, to which a catalytic amount of TEMPO has been added. Then at a constant pH and at a temperature between -10 and 100°C, preferably between -5 and 20°C, an oxidizing agent, for instance a solution of sodium hypochlorite, preferably in the presence of a catalytic amount of sodium bromide, in water, is
35 added dropwise or batchwise, with stirring. If sodium hypochlorite is used as oxidizing agent, the pH will usually be in the range of about 5 to 13, preferably from about 8 to

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10. The pH is preferably 9-11.5 if sodium hypochlorite is used in the presence of a catalytic amount of sodium bromide. The pH is maintained constant by dripping to the reaction mixture a base or a solution thereof in water, for instance an aqueous
5 1 M sodium hydroxide, potassium hydroxide or sodium hydrogen carbonate solution.

The oxidation reaction has gone to completion when no consumption of base occurs anymore. If desired, only a part of the primary hydroxyl groups present can be oxidized. This can
10 be effected by adding less oxygen donor, for instance hypochlorite, and/or discontinuing the reaction by adding an (excess of a) quenching substance such as methanol or ethanol. This is within reach of those skilled in the art.

In a preferred embodiment of the method according to the
15 invention, in which more than 95% of the primary hydroxyl groups present in the starting material is oxidized, the reaction is continued until substantially no consumption of the oxidizing agent occurs anymore.

The use of sodium hypochlorite alone as oxidant leads to
20 a high product selectivity, but to a relatively low reaction rate. If a catalytic amount of sodium bromide is added, so that sodium hypobromite is formed in situ, the reaction rate increases appreciably, but the selectivity is lower. The fact is, in the last-mentioned case there also occurs some extent
25 of diol cleavage. However, when carbohydrate ethers with a DS greater than about 0.5, preferably about 1, are used, this side reaction hardly occurs anymore, because then there are virtually no anhydroglucose units left that still contain unsubstituted hydroxyl groups at the C(2)- and C(3)-atom.

30 Oxidized carbohydrate ethers with a good sequestering activity can also be obtained, for instance, by oxidizing starch to polyglucuronic acid, followed by a carboxymethylation step. With polyglucuronic acid, there is also the possibility of hydroxyethylation and subsequent
35 oxidation. Thus, oxidized carbohydrate ethers are obtained which have a similar structure to the compounds etherified directly.

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It is noted there are also methods known in which the oxidation can take place at a lower pH, though with other oxidants than hypohalogenites.

Finally, the invention relates to the use of an oxidized carbohydrate ether or a mixture of two or more oxidized carbohydrate derivatives according to the invention or manufactured by the methods according to the invention, as sequestering agent or anticrustation agent. Preferably, the oxidized carbohydrate ethers concerned are used as an ingredient in washing powders or liquid detergent formulations, washing-up liquid formulations, or other cleaning agents.

The invention is further elucidated in and by the examples below. These non-limiting examples illustrate a number of aspects of the invention. For instance, the calcium-binding capacity is determined as a measure for the activity of the compounds. Also, some comparative examples have been included.

Wherever in the description mention is made of percentages, they are understood to be percentages by weight based on the weight of the total composition, unless stated otherwise.

In the examples, the following abbreviations are used:

d.s. = dry substance content
EtOH = ethanol
MeOH = methanol
DS = degree of substitution
MS = degree of molar substitution

Reference to MS will be made if the substituents themselves contain reactive centers at which substitution can occur as well. As a result, there is no direct correlation between the number of substituents and the number of substituted hydroxyl groups on the anhydroglucopyranosations. In these derivatives the DS is therefore equal to or lower than the MS.

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The carboxyl content (in milli-equivalents per gram dry product) was determined in all cases on the basis of the amount of lye in the form of a 0.1 N sodium hydroxide solution required to adjust a solution of 0.50 g of the product under investigation in 60 ml demineralized water, whose pH had priorly been adjusted to 2.00 using a 4.0 N HCl solution, to a pH of 11.50, minus the amount of lye required to adjust a solution of the corresponding starting material (likewise 0.50 g in 60 ml demineralized water, whose pH had priorly been adjusted to 2.00 using a 4.0 N HCl solution) to a pH of 11.50. In those cases where a carboxymethyl ether was used as starting material, the value of the corresponding non-substituted polysaccharide was taken as control.

The calcium-binding capacity was measured as follows, according to a conventional method. In 200 ml demineralized water the Ca-hardness was adjusted to 15° DH (German Hardness) by addition of 78.7 mg $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The solution was buffered with 0.2 g borax. As soon as the potential (measured with a calcium ion selective electrode) remained constant, the solution was titrated in steps (in portions of 5 or 10 ml) with a 1% solution of the sample examined, each addition being followed by a waiting period until the reading was stable. The $[\text{Ca}^{2+}]$ corresponding with each potential value was determined separately with a calibration curve.

Reference is made to Figs. 1-12. In Figs. 1-6 the calcium-binding capacities of products according to the invention are represented. The increase of the calcium-binding capacity as a function of the degree of oxidation is shown in Figs. 7-10. Fig. 11 shows that the calcium-binding capacity upon continued oxidation increases faster than would expected solely on the ground of the measured carboxyl content. Fig. 12 shows the calcium-binding capacity of some products that were obtained by etherification of polyglucuronic acid.

Instead of referring to calcium-binding capacity, the literature also refers to sequestering capacity (SC). The SC is expressed as the reciprocal of the amount of sample (in

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grams) required to reduce the $[Ca^{2+}]$ of 200 ml solution from 10^{-3} to 10^{-5} mol/l.

The sequestering capacity has been calculated for all products and is shown in Table 1, along with the sequestering capacities of some comparative compounds. In Tables 2-5 the sequestering capacity is represented as a function of the degree of oxidation.

Comparative Example 1:

Oxidation of potato starch with TEMPO/NaOCl/NaBr

10 25.00 g Native potato starch (d.s. 86.90%, 134 mmol; AVEBE) was suspended with stirring in 50 ml water, to which 0.13 g TEMPO (0.83 mmol; Aldrich-Chemie) and 1.00 g NaBr (9.7 mmol) had been added. The pH of the suspension was adjusted to 10.8 by addition of a 1 M sodium hydroxide solution. Then at a temperature of 0°C, 135 ml of a solution of NaOCl in water (content 145-150 g/l, approx. 277 mmol) was added dropwise with stirring over a period of 30 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution (pH-stat). After 1 more hour of stirring, virtually no lye was consumed anymore (total consumption 130.5 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 1000 ml EtOH, filtered, washed with 80% EtOH/H₂O and dried in air. Yield 34.73 g α-polyglucuronic acid (d.s. 84.08%, carboxyl content 4.3 meq/g). The theoretical yield was 31.56 g; so the product still contained salt.

Comparative Example 2:

Oxidation of potato amylose with TEMPO/NaOCl/NaBr

30 25.02 g Amylose-V (d.s. 89.12%, 138 mmol; AVEBE) was suspended, with stirring, in 100 ml water, to which 0.13 g TEMPO (0.83 mmol) and 1.02 g NaBr (9.9 mmol) had been added. The pH of the suspension was adjusted to 10.8 using 1 M sodium hydroxide solution. Then at a temperature of 0°C, 130 ml of a

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solution of NaOCl in water (content 145-150 g/l, approx. 267 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another hour, there was virtually no consumption of lye anymore (total consumption 145.6 ml); the reaction was considered complete. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 1000 ml EtOH, filtered, washed with 80% EtOH/H₂O and dried in air. Yield 32.81 g α -polyglucuronic acid (d.s. 84.02%, carboxyl content 4.5 meq/g). The theoretical yield was 32.52 g, the product still contained salt.

Comparative Example 3:

15 Oxidation of cellulose with TEMPO/NaOCl/NaBr

22.38 g Cellulose (d.s. 93.96%, 130 mmol; Merck-Schuchard) was suspended, with stirring, in 50 ml water, to which 0.10 g TEMPO (0.64 mmol) and 1.00 g NaBr (9.7 mmol) had been added. The pH of the suspension was adjusted to 10.8 using 1 M sodium hydroxide solution. Then at a temperature of 0°C, 138 ml of a solution of NaOCl in water (content 145-150 g/l, approx. 283 mmol) was added dropwise, with stirring, over a period of 1 hour. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another 20 hours, there was virtually no consumption of lye anymore (total consumption 142.0 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 1000 ml EtOH, filtered, washed with 80% EtOH/H₂O and dried in the air. Yield 33.32 g β -polyglucuronic acid (d.s. 85.42%, carboxyl content 4.1 meq/g). The theoretical yield was 30.13 g, the product still contained salt.

Comparative Example 4:

Oxidation of chitin (poly- α -1,4-[2-(N-acetylamino)-2-deoxy-D-glucose])

- 4.86 g Chitin (d.s. 91.36%, 18.4 mmol; Fluka AG) was
5 suspended, with stirring, in 50 ml water, to which 0.09 g
TEMPO (0.58 mmol) and 0.54 g NaBr (5.2 mmol) had been added.
The pH of the suspension was adjusted to 10.8 using 1M sodium
hydroxide solution. Then at a temperature of 0°C, 25 ml of a
solution of NaOCl in water (content 145-150 g/l,
10 approx. 51 mmol) was added dropwise with stirring over a
period of 45 minutes. The pH was maintained at a constant
value of 10.8 by the addition of 1 M sodium hydroxide solution
(pH-stat). After stirring for another 2 hours, there was
virtually no consumption of lye anymore (total consumption
15 34.1 ml); the reaction was considered complete. The clear
solution obtained was then neutralized to pH = 7.0 using 0.5 M
hydrochloric acid, poured out in 500 ml EtOH, filtered, washed
with a 70% EtOH solution and dried in the air. Yield 4.60 g
oxidized chitin (d.s. 84.22%, carboxyl content 3.3 meq/g).
20 The carboxyl content found was lower than expected,
probably as a result of the deactivation of the catalyst by
the free amino groups present in small amounts in chitin.

Comparative Example 5:

Oxidation of polyglucuronic acid with NaOCl/NaBr

- 25 5.01 g polyglucuronic acid (d.s. 84.02%, 21.3 mmol, CZ
4.5 meq/g) prepared according to the method according to
Example 1, was dissolved with stirring in 50 ml water, to
which 0.28 g NaBr (2.7 mmol) had been added. The pH of the
solution was adjusted to 9.5 using 1 M sodium hydroxide
30 solution. Then at a temperature of 0°C, 30 ml of a solution of
NaOCl in water (content 145-150 g/l, approx. 61.5 mmol) was
added dropwise, with stirring, over a period of 30 minutes.
The pH was maintained at a constant value of 9.5 by addition
of 1 M sodium hydroxide solution (pH-stat). After stirring for

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another 20 hours there was virtually no consumption of lye anymore (total consumption 22.14 ml); the reaction was considered complete. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured
5 out in 500 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried at 50°C (vented oven). Yield 3.99 g dicarboxypolyglucuronic acid (d.s. 96.17%, carboxyl content 6.3 meq/g).

Example 1:

10 Oxidation of carboxymethyl starch

a) 5.03 g Carboxymethyl starch (d.s. 94.83%, DS_{max} 0.1, 28.1 mmol; AVEBE) was dissolved with stirring in 100 ml water to which 0.07 g TEMPO (0.45 mmol) and 0.25 g NaBr (2.4 mmol) had been added. The pH of the suspension was adjusted to 10.8
15 using 1 M sodium hydroxide solution. Then at a temperature of 0°C, 26 ml of a solution of NaOCl in water (content 145-150 g/l, approx. 53 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium
20 hydroxide solution (pH-stat). After stirring for another hour, there was virtually no consumption of lye anymore (total consumption 22.5 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml EtOH,
25 filtered, washed with a 70% EtOH solution and dried at 60°C (vented oven). Yield 5.73 g oxidized carboxymethyl starch (d.s. 94.36%, carboxyl content 4.8 meq/g).

b) In the same manner as under a) 5.01 g carboxymethyl starch (d.s. 93.89%, DS_{max} = 0.5, 23.2 mmol) was oxidized
30 (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.27 g NaBr (2.6 mmol), 24 ml NaOCl solution (approx. 49 mmol), 20.3 ml sodium hydroxide solution). Yield 5.10 g oxidized carboxymethyl starch (d.s. 94.11%, carboxyl content 6.0 meq/g).

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- c) In the same manner as under a) 5.04 g carboxymethyl starch (d.s. 94.35%, $DS_{max} = 1.0$, 19.6 mmol) was oxidized (amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.25 g NaBr (2.4 mmol), 19 ml NaOCl solution (approx. 39 mmol), 15.4 ml sodium hydroxide solution). Yield 4.35 g oxidized carboxymethyl starch (d.s. 93.65%, carboxyl content 5.8 meq/g).

Example 2:

Oxidation of hydroxyethyl starch

- 10 a) 5.03 g Hydroxyethyl starch (d.s. 88.77%, MS 0.34, 25.2 mmol; AVEBE) was dissolved, with stirring, in 100 ml water, to which had been added 0.07 g TEMPO (0.45 mmol) and 0.27 g NaBr (2.6 mmol). The pH of the suspension was adjusted to 10.8 using 1 M sodium hydroxide solution. Then at a
15 temperature of 0°C, 32 ml of a solution of NaOCl in water (approx. 65 mmol) was added dropwise, with stirring, over a period of 45 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another hour, virtually no lye
20 was consumed anymore (total consumption 30.75 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried in the air. Yield 5.11 g oxidized
25 hydroxyethyl starch (d.s. 82.85%, carboxyl content 3.8 meq/g).
- b) In the same manner as under a) 5.02 g hydroxyethyl starch (d.s. 89.68%, MS 0.85, 22.5 mmol) was oxidized (amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.30 g NaBr (2.9 mmol), 34 ml NaOCl solution (approx. 69 mmol, added over
30 a period of 1 hour), 29.20 ml sodium hydroxide solution). Yield 6.36 g oxidized hydroxyethyl starch (d.s. 80.56%, carboxyl content 4.6 meq/g).
- c) In the same manner as under a) 5.02 g hydroxyethyl starch (d.s. 88.87%, MS 1.20, 20.7 mmol) was oxidized
35 (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.28 g NaBr

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(2.7 mmol), 36 ml NaOCl solution (approx. 74 mmol), 31.0 ml sodium hydroxide solution). Yield 5.21 g oxidized hydroxyethyl starch (d.s. 78.67%, carboxyl content 4.5 meq/g).

Example 3:

5 Oxidation of hydroxyethyl cellulose

a) 5.02 g Hydroxyethyl cellulose (d.s. 90.75%, MS 1.64, 19.3 mmol; Aqualon) was dissolved, with stirring, in 100 ml water, to which had been added 0.05 g TEMPO (0.32 mmol) and 0.27 g NaBr (2.6 mmol). The pH of the suspension was adjusted
10 to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 37 ml of a solution of NaOCl in water (approx. 75 mmol) was added dropwise, with stirring, over a period of 1.5 hours. The pH was maintained at a constant value by addition of 1 M sodium hydroxide solution (pH-stat). After
15 stirring for another four hours, virtually no lye was consumed anymore (total consumption 36.11 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using a 4.0 M hydrochloric acid,
20 poured out in 500 ml MeOH, filtered, washed with 80% acetone/H₂O and dried in the air. Yield 3.83 g oxidized hydroxyethyl cellulose (d.s. 83.05%, carboxyl content 5.8 meq/g).

b) In the same manner as under a) 5.00 g hydroxyethyl cellulose (d.s. 91.57%, MS 3.23, 14.9 mmol) was oxidized
25 (amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.27 g NaBr (2.9 mmol), 40 ml NaOCl solution (approx. 82 mmol, added over a period of 1 hour), 34.35 ml sodium hydroxide solution (stirring for 16 hours)). After neutralization with 4.0 M hydrochloric acid, the solution was poured out in 800 ml
30 MeOH/acetone (5:3), filtered, washed with acetone/H₂O and dried in the air. Yield 3.37 g oxidized hydroxyethyl cellulose (d.s. 85.45%, carboxyl content 5.2 meq/g).

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Example 4:

Oxidation of carboxymethyl cellulose

5.00 g Carboxymethyl cellulose (d.s. 87.42%; DS 0.5, 21.6 mmol; AKU) was dissolved, with stirring, in 150 ml water, to which had been added 0.05 g TEMPO (0.32 mmol) and 0.24 g NaBr (2.3 mmol). The pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 25 ml of a solution of NaOCl in water (approx. 51 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another 6 hours, virtually no lye was consumed anymore (total consumption 24.11 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with MeOH/H₂O and dried in the air. Yield 5.80 g oxidized carboxymethyl cellulose (d.s. 84.00%, carboxyl content 6.2 meq/g).

Example 5:

Oxidation of cyanoethyl starch

10.05 g Cyanoethyl starch (d.s. 91.80%, DS 0.5, 48.9 mmol; AVEBE) was suspended, with stirring, in 100 ml water, to which had been added 0.10 g TEMPO (0.64 mmol) and 0.50 g NaBr (4.9 mmol). The pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 60 ml of a solution of NaOCl in water (approx. 123 mmol) was added dropwise, with stirring, over a period of 45 minutes. The pH was maintained at a constant value by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another hour, there was virtually no consumption of lye anymore (total consumption 51.04 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 600 ml MeOH, filtered, washed with

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MeOH/H₂O and dried in the air. Yield 10.89 g oxidized cyanoethyl starch (d.s. 82.91%, carboxyl content 3.7 meq/g).

Example 6:

Oxidation of 2-nitrobutyl starch

5 10.04 g 2-Nitrobutyl starch (d.s. 86.59%, MS 0.11, 50.0 mmol), prepared according to the method of Example 19 of NL-A-9401811, was suspended, with stirring, in 100 ml water, to which had been added 0.10 g TEMPO (0.64 mmol) and 0.51 g NaBr (5.0 mmol). The pH of the suspension was adjusted
10 to 10.8 with a 1 M sodium hydroxide solution. Then at a temperature of 0°C 50 ml of a solution of NaOCl in water (approx. 123 mmol) was added dropwise, with stirring, over a period of 60 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution
15 (pH-stat). After stirring for another hour, there was virtually no consumption of lye anymore (total consumption 40.53 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 600 ml MeOH, filtered, washed
20 with MeOH/H₂O and dried in the air. Yield 11.01 g oxidized 2-nitrobutyl starch (d.s. 84.16%, carboxyl content 2.4 meq/g).

Example 7:

Oxidation of dihydroxypropyl amylose

2.05 g Dihydroxypropyl amylose (MS approx. 1.0, approx. 8 mmol) analogous to the method of Zhang et al. (J. Macromol. Sci.- Chem., A25, 1988, 955) prepared through alkaline etherification of amylose with chloropropanediol, was dissolved, with stirring, in 75 ml H₂O, to which had been added 0.04 g TEMPO (0.25 mmol) and 0.14 g NaBr (1.4 mmol). The
30 pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 35 ml of a solution of NaOCl in water (approx. 72 mmol) was added dropwise, with stirring, over a period of 60 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M

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sodium hydroxide solution (pH-stat). After stirring for another 6 hours, there was virtually no consumption of lye anymore (total consumption 39.25 ml); the reaction was considered completed. The clear solution obtained was then
5 neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 600 ml MeOH, filtered, washed with MeOH/H₂O and dried in the air. Yield 1.90 g oxidized dihydroxypropyl amylose (d.s. 90.75%, carboxyl content 6.9 meq/g).

Example 8:

10 Oxidation of hydroxypropyl starch

a) 5.01 g Hydroxypropyl starch (d.s. 97.92%, MS_{max} 0.5, 25.7 mmol; AVEBE) was dissolved, with stirring, in 100 ml water to which had been added 0.06 g TEMPO (0.38 mmol) and 0.28 g NaBr (2.7 mmol). The pH of the suspension was adjusted
15 to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 29 ml of a solution of NaOCl in water (approx. 59 mmol) was added dropwise, with stirring, over a period of 60 minutes. The pH was maintained at a constant value by addition of 1 M sodium hydroxide solution (pH-stat).
20 After stirring for another hour, there was virtually no consumption of lye anymore (total consumption 27.02 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with 80%
25 MeOH/H₂O and dried in the air. Yield 5.54 g oxidized hydroxypropyl starch (d.s. 85.80%, carboxyl content 3.7 meq/g).

b) In the same manner as under a) 4.98 g hydroxypropyl starch (d.s. 96.53%, MS_{max} = 1.0, 21.8 mmol) was oxidized
30 (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.25 g NaBr (2.4 mmol), 24 ml NaOCl solution (approx. 49 mmol, added over a period of 30 minutes), 21.64 ml sodium hydroxide solution (stirring for 1 hour)). Yield 3.66 g oxidized hydroxypropyl starch (d.s. 86.07%, carboxyl content 2.7 meq/g).

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c) In the same manner as under a) 5.01 g hydroxypropyl starch (d.s. 96.11%, $MS_{max} = 1.20$, 19.3 mmol) was oxidized (amounts, respectively, 0.08 g TEMPO (0.51 mmol), 0.24 g NaBr (2.3 mmol), 20.5 ml NaOCl solution (approx. 42 mmol), 18.63 ml sodium hydroxide solution (stirring for 1 hour)). Yield 2.51 g oxidized hydroxypropyl starch (d.s. 88.33%, carboxyl content 2.0 meq/g).

Table 1 lists the sequestering capacities (SC) and the carboxyl contents (CZ, in meq/g) of the polysaccharides/poly-saccharide ethers oxidized in Examples V1-V5, 1-8 and 13-14.

Table 1

Sequestering capacity (SC, g⁻¹) and carboxyl
content (CZ, meq/g) of oxidized
polysaccharides/polysaccharide ethers

5	Example number	SC	CZ
	Sodium tripolyphosphate (PH)	7.2	--
10	EDTA	10.0	13.7
	V1	0.7	4.3
	V2	1.0	4.5
	V3	0.9	4.1
	V4	0.6	3.3
15	V5	3.1	6.3
	1a	1.1	4.8
	1b	2.1	6.0
	1c	2.1	5.8
	2a	0.6	3.8
20	2b	1.3	4.6
	2c	1.7	4.5
	3a	1.7	5.8
	3b	1.9	5.2
	4	1.2	6.2
25	5	1.1	3.7
	6	1.2	2.4
	7	2.9	6.9
	8a	0.9	3.7
	8b	0.8	2.7
30	8c	0.3	2.0
	13	2.3	5.8
	14a	1.1	3.9
	14b	3.6	6.9

Example 9:

Sequestering capacity of oxidized carboxymethyl starch (DS_{\max} 0.5) as a function of the degree of oxidation

a) 5.01 g Carboxymethyl starch (d.s. 93.89%, DS_{\max} 0.5, 23.3 mmol) was dissolved, with stirring, in 100 ml H_2O , to which had been added 0.05 g TEMPO (0.32 mmol) and 0.28 g NaBr (2.7 mmol). The pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 15 ml of a solution of NaOCl in water (approx. 31 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another hour, there is virtually no consumption of lye anymore (total consumption 12.52 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with 80% MeOH/ H_2O and dried in the air. Yield 4.62 g oxidized carboxymethyl starch (d.s. 83.17%, carboxyl content 4.6 meq/g).

b) In the same manner as under a) 5.05 g carboxymethyl starch (d.s. 93.89%, MS_{\max} = 1.0, 21.8 mmol) was oxidized (amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.28 g NaBr (2.7 mmol), 20 ml NaOCl solution (approx. 41 mmol, added over a period of 30 minutes), 16.20 ml sodium hydroxide solution (stirring for 1.5 hours)). Yield 5.40 g oxidized carboxymethyl starch (d.s. 80.32%, carboxyl content 5.7 meq/g).

c) In the same manner as under a) 5.04 g carboxymethyl starch (d.s. 93.89%, MS_{\max} = 1.0, 21.8 mmol) was oxidized (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.30 g NaBr (2.9 mmol), 25 ml NaOCl solution (approx. 51 mmol, added over a period of 30 minutes), 22.89 ml sodium hydroxide solution (stirring for 1.5 hours)). Yield 5.80 g oxidized carboxymethyl starch (d.s. 81.47%, carboxyl content 6.2 meq/g).

d) In the same manner as under a) 5.03 g carboxymethyl starch (d.s. 93.89%, MS_{\max} = 1.0, 21.8 mmol) was oxidized

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(amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.30 g NaBr (2.9 mmol), 30 ml NaOCl solution (approx. 62 mmol, added over a period of 30 minutes), 29.99 ml sodium hydroxide solution (stirring for 16 hours)). Yield 5.89 g oxidized carboxymethyl starch (d.s. 83.01%, carboxyl content 6.6 meq/g).

e) In the same manner as under a) 5.06 g carboxymethyl starch (d.s. 93.89%, $MS_{max} = 1.0$, 21.8 mmol) was oxidized (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.27 g NaBr (2.6 mmol), 35 ml NaOCl solution (approx. 72 mmol, added over a period of 30 minutes), 36.79 ml sodium hydroxide solution (stirring for 6 hours)). Yield 5.57 g oxidized carboxymethyl starch (d.s. 82.87%, carboxyl content 7.2 meq/g).

Table 2

Sequestering capacities (SC) and carboxyl content (CZ) of oxidized carboxymethyl starch (DS_{max} 0.5)

Carboxymethyl starch	SC, g^{-1}	CZ, meq/g	SC/CZ
9a	0.8	4.6	0.17
9b	1.3	5.7	0.23
9c	2.5	6.2	0.40
9d	3.65	6.6	0.53
9e	6.8	7.2	0.94

Example 10:

Sequestering capacity of oxidized carboxymethyl starch
(DS_{max} 1.0) as a function of the degree of oxidation

- a) 5.05 g Carboxymethyl starch (d.s. 94.35%, DS_{max} 1.0, 19.7 mmol) was dissolved, with stirring, in 100 ml water, to which had been added 0.06 g TEMPO (0.38 mmol) and 0.27 g NaBr (2.6 mmol). The pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 15 ml of a solution of NaOCl in water (approx. 31 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another 1 hour, virtually no consumption of lye occurred anymore (total consumption 13.62 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried in the air. Yield 4.84 g oxidized carboxymethyl starch (d.s. 79.42%, carboxyl content 4.3 meq/g).
- b) In the same manner as under a) 5.03 g carboxymethyl starch (d.s. 94.35%, DS_{max} = 1.0, 19.6 mmol) was oxidized (amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.28 g NaBr (2.7 mmol), 20 ml NaOCl solution (approx. 41 mmol, added over a period of 30 minutes), 19.19 ml sodium hydroxide solution (stirring for 1 hour)). Yield 4.65 g oxidized carboxymethyl starch (d.s. 81.83%, carboxyl content 5.8 meq/g).
- c) In the same manner as under a) 5.03 g carboxymethyl starch (d.s. 94.35%, DS_{max} = 1.0, 19.6 mmol) was oxidized (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.28 g NaBr (2.7 mmol), 25 ml NaOCl solution (approx. 51 mmol, added over a period of 30 minutes), 24.33 ml sodium hydroxide solution (stirring for 2.5 hours)). Yield 4.95 g oxidized carboxymethyl starch (d.s. 81.67%, carboxyl content 6.7 meq/g).
- d) In the same manner as under a) 5.03 g carboxymethyl starch (d.s. 94.35%, DS_{max} = 1.0, 19.6 mmol) was oxidized

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(amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.30 g NaBr (2.9 mmol), 30 ml NaOCl solution (approx. 62 mmol, added over a period of 30 minutes), 33.60 ml sodium hydroxide solution (stirring for 24 hours)). Yield 4.90 g oxidized carboxymethyl starch (d.s. 81.74%, carboxyl content 7.4 meq/g).

e) In the same manner as under a) 5.05 g carboxymethyl starch (d.s. 94.35%, $DS_{max} = 1.0$, 19.7 mmol) was oxidized (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.27 g NaBr (2.6 mmol), 35 ml NaOCl solution (approx. 72 mmol, added over a period of 30 minutes), 40.79 ml sodium hydroxide solution (stirring for 16 hours)). Yield 4.94 g oxidized carboxymethyl starch (d.s. 82.10%, carboxyl content 7.9 meq/g).

Table 3

Sequestering capacities (SC) and carboxyl content (CZ) of oxidized carboxymethyl starch (DS_{max} 1.0)

Carboxymethyl starch	SC, g^{-1}	CZ meq/g	SC/CZ
10a	1.6	4.3	0.37
10b	2.6	5.8	0.44
10c	4.1	6.7	0.61
10d	4.9	7.4	0.66
10e	6.3	7.9	0.80

Example 11: Sequestering capacity of oxidized hydroxyethyl starch (MS_{\max} 1.0) as a function of the degree of oxidation

a) 5.06 g Hydroxyethyl starch (d.s. 95.31%, MS_{\max} = 1.0, 23.3 mmol) was dissolved, with stirring, in 100 ml water, to which had been added 0.05 g TEMPO (0.32 mmol) and 0.33 g NaBr (3.2 mmol). The pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 30 ml of a solution of NaOCl in water (approx. 62 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another hour, there is virtually no consumption of lye anymore (total consumption 28.52 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried in the air. Yield 4.23 g oxidized hydroxyethyl starch (d.s. 84.10%, carboxyl content 39 meq/g).

b) In the same manner as under a) 5.02 g hydroxyethyl starch (d.s. 95.31%, MS_{\max} = 1.0, 23.2 mmol) was oxidized (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.28 g NaBr (2.7 mmol), 40 ml NaOCl solution (approx. 82 mmol, added over a period of 1 hour), 38.50 ml sodium hydroxide solution (stirring for 2 hours)). Yield 5.63 g oxidized hydroxyethyl starch (d.s. 79.69%, carboxyl content 4.0 meq/g).

c) In the same manner as under a) 5.02 g hydroxyethyl starch (d.s. 95.31%, MS_{\max} = 1.0, 23.2 mmol) was oxidized (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.33 g NaBr (3.2 mmol), 50 ml NaOCl solution (approx. 103 mmol, added over a period of 1 hour), 46.85 ml sodium hydroxide solution (stirring for 20 hours)). Yield 6.63 g oxidized hydroxyethyl starch (d.s. 82.19%, carboxyl content 5.5 meq/g).

d) In the same manner as under a) 5.00 g hydroxyethyl starch (d.s. 95.31%, MS_{\max} = 1.0, 23.2 mmol) was oxidized (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.32 g NaBr

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(3.1 mmol), 60 ml NaOCl solution (approx. 123 mmol, added over a period of 1.5 hours), 58.12 ml sodium hydroxide solution (stirring for 6 hours)). Yield 6.76 g oxidized hydroxyethyl starch (d.s. 82.38%, carboxyl content 6.5 meq/g).

- 5 e) In the same manner as under a) 5.01 g hydroxyethyl starch (d.s. 95.31%, $MS_{max} = 1.0$, 23.2 mmol) was oxidized (amounts, respectively, 0.06 g TEMPO (0.38 mmol), 0.31 g NaBr (3.0 mmol), 70 ml NaOCl solution (approx. 144 mmol, added over a period of 1.5 hours), 70.42 ml sodium hydroxide solution
10 (stirring for 20 hours)). Yield 6.34 g oxidized hydroxyethyl starch (d.s. 82.99%, carboxyl content 7.2 meq/g).

Table 4

Sequestering capacities (SC) and carboxyl content (CZ)
of oxidized hydroxyethyl starch ($MS_{max} 1.0$)

15 Carboxymethyl starch	SC, g^{-1}	CZ, meq/g	SC/CZ
11a	0.7	3.9	0.18
11b	1.2	4.0	0.30
20 11c	2.3	5.5	0.42
11d	4.3	6.5	0.66
11e	4.6	7.2	0.64

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Example 12:

Sequestering capacity of oxidized carboxymethyl cellulose (DS 0.5) as a function of the degree of oxidation

a) 5.00 g Carboxymethyl cellulose (d.s. 87.42%, DS 1.0, 21.6 mmol) was dissolved, with stirring, in 150 ml water, to which had been added 0.04 g TEMPO (0.26 mmol) and 0.24 g NaBr (2.3 mmol). The pH of the suspension was adjusted to 10.8 with 1 M sodium hydroxide solution. Then at a temperature of 0°C 15 ml of a solution of NaOCl in water (approx. 31 mmol) was added dropwise, with stirring, over a period of 30 minutes. The pH was maintained at a constant value of 10.8 by addition of 1 M sodium hydroxide solution (pH-stat). After stirring for another hour, there was virtually no consumption of lye anymore (total consumption 13.18 ml); the reaction was considered completed. The clear solution obtained was then neutralized to pH = 7.0 using 4.0 M hydrochloric acid, poured out in 500 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried at 50°C (vented oven). Yield 4.94 g oxidized carboxymethyl cellulose (d.s. 95.72%, carboxyl content 4.7 meq/g).

b) In the same manner as under a) 5.02 g carboxymethyl cellulose (d.s. 87.42%, DS 1.0, 21.6 mmol) was oxidized (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.25 g NaBr (2.4 mmol), 20 ml NaOCl solution (approx. 41 mmol, added over a period of 30 minutes), 19.27 ml sodium hydroxide solution (stirring for 2 hours)). Yield 5.72 g oxidized carboxymethyl cellulose (d.s. 96.34%, carboxyl content 4.7 meq/g).

c) In the same manner as under a) 5.00 g carboxymethyl cellulose (d.s. 87.42%, DS 1.0, 21.6 mmol) was oxidized (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.25 g NaBr (2.4 mmol), 25 ml NaOCl solution (approx. 51 mmol, added over a period of 30 minutes), 24.11 ml sodium hydroxide solution (stirring for 6 hours)). Yield 5.80 g oxidized carboxymethyl cellulose (d.s. 84.00%, carboxyl content 6.2 meq/g).

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d) In the same manner as under a) 5.00 g carboxymethyl cellulose (d.s. 87.42%, DS 1.0, 21.6 mmol) was oxidized (amounts, respectively, 0.07 g TEMPO (0.45 mmol), 0.27 g NaBr (2.6 mmol), 30 ml NaOCl solution (approx. 62 mmol, added over a period of 30 minutes), 32.25 ml sodium hydroxide solution (stirring for 16 hours)). Yield 5.64 g oxidized carboxymethyl cellulose (d.s. 85.66%, carboxyl content 6.9 meq/g).

e) In the same manner as under a) 5.00 g carboxymethyl cellulose (d.s. 87.42%, DS 1.0, 21.6 mmol) was oxidized (amounts, respectively, 0.05 g TEMPO (0.32 mmol), 0.23 g NaBr (2.2 mmol), 35 ml NaOCl solution (approx. 72 mmol, added over a period of 1 hour), 41.07 ml sodium hydroxide solution (stirring for 72 hours)). Yield 5.49 g oxidized carboxymethyl cellulose (d.s. 83.98%, carboxyl content 7.2 meq/g).

Table 5

Sequestering capacities (SC) and carboxyl content (CZ) of oxidized carboxymethyl cellulose (DS 0.5)

Carboxymethyl cellulose	SC, g ⁻¹	CZ, meq/g	SC/CZ
12a	0.7	4.7	0.15
12b	0.7	4.7	0.15
12c	1.2	6.2	0.19
12d	2.2	6.9	0.32
12e	2.7	7.2	0.38

Example 13:

Synthesis of carboxymethylpolyglucuronic acid

20.12 g polyglucuronic acid (d.s. 94.73%, carboxyl content 4.1 meq/g) is dissolved in 50 ml 25% NaOH solution. At
5 T = 60°C 15.04 g sodium chloroacetate (0.13 mol) is added to the solution. After 75 minutes the solution is neutralized to pH 7.0 with a 4.0 M HCl solution, poured out in 500 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried at T = 50°C (vented oven). Yield 20.95 g carboxymethylpolyglucuronic acid
10 (d.s. 94.70%, carboxyl content 5.8 meq/g).

Example 14a:

Synthesis of hydroxyethylpolyglucuronic acid

4.96 g polyglucuronic acid (d.s. 94.73%, carboxyl content 4.1 meq/g) is dissolved in 50 ml 4.4% NaOH solution.
15 To the solution [at] 1.6 g ethylene oxide (36.3 mmol) in 1.5 ml H₂O is dropped. After 2 hours of stirring at T = 50°C the solution is neutralized to pH = 7 with a 4.0 M HCl solution, poured out in 300 ml MeOH, filtered, washed with 80% MeOH/H₂O and dried at T = 50°C (vented oven). Yield 4.48 g
20 hydroxyethylpolyglucuronic acid (d.s. 95.01%, carboxyl content 3.9 meq/g).

Example 14b:

Oxidation of hydroxyethylpolyglucuronic acid

2.48 g of hydroxyethylpolyglucuronic acid (d.s. 95.01%,
25 carboxyl content 3.9 meq/g) is dissolved in 30 ml H₂O, to which have been added 0.03 TEMPO (0.19 mmol) and 0.12 g NaBr (1.2 mmol). The pH of the suspension is adjusted to 10.8 using a 1 M NaOH solution. Then at a temperature of 0°C 10 ml of a solution of NaOCl in water (approx. 21 mmol) is added
30 dropwise, with stirring, over a period of 45 minutes. The pH is maintained at a constant value of 10.8 by addition of 1 M NaOH solution (pH-stat). After stirring for another 2.5 hours, there is virtually no consumption of lye anymore (total

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consumption 8.34 ml); the reaction is considered completed. The clear solution obtained is then neutralized to pH = 7.0 using a 4.0 M HCl solution, poured out in 200 ml MeOH, filtered, washed with MeOH/H₂O and dried in the air. Yield

5 2.69 g oxidized hydroxyethylpolyglucuronic acid (d.s. 82.4%, carboxyl content 6,9 meq/g).

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CLAIMS

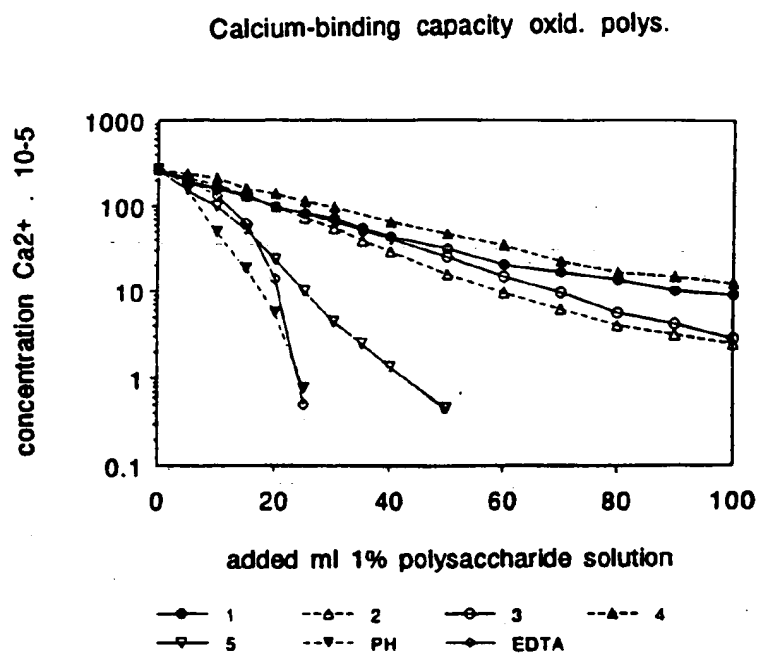
1. Oxidized polymeric carbohydrate ethers or mixtures thereof having an average degree of polymerization of at least 10.
2. Oxidized polymeric carbohydrate ethers according to claim 1, wherein the polymeric carbohydrate ethers have been oxidized to so large an extent that multidentate conformations can form.
3. Oxidized polymeric carbohydrate ethers according to claim 1 or 2, with a carboxyl content of at least 5 milli-equivalents per gram and a sequestering capacity of at least 2 g⁻¹.
4. Oxidized carbohydrate ethers according to any one of claims 1-3, with a degree of substitution DS between 0 and 2.
5. A method for the preparation of oxidized carbohydrate ethers, wherein at least a part of the primary hydroxyl groups of polymeric carbohydrate ethers with a degree of polymerization of at least 10 is selectively oxidized.
6. A method according to claim 5, wherein the oxidation reaction is carried out utilizing a catalytic amount of stable nitroxide radicals in the presence of a suitable oxygen donor.
7. A method according to claim 5 or 6, wherein 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) is used as stable nitroxide radical and sodium hypochlorite, optionally in combination with sodium bromide, as oxygen donor.
8. A method according to any one of claims 5-7, wherein more than 95% of the primary hydroxyl groups present in the starting material is oxidized by continuing the reaction until substantially no consumption of the oxidizing agent occurs anymore.
9. Use of an oxidized carbohydrate ether or a mixture of two or more oxidized carbohydrate derivatives according to any one of claims 1-4 as sequestering agent or anticrustation agent.

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10. Use of oxidized carbohydrate ethers according to claim 9 as an ingredient of washing powders or liquid detergent formulations.

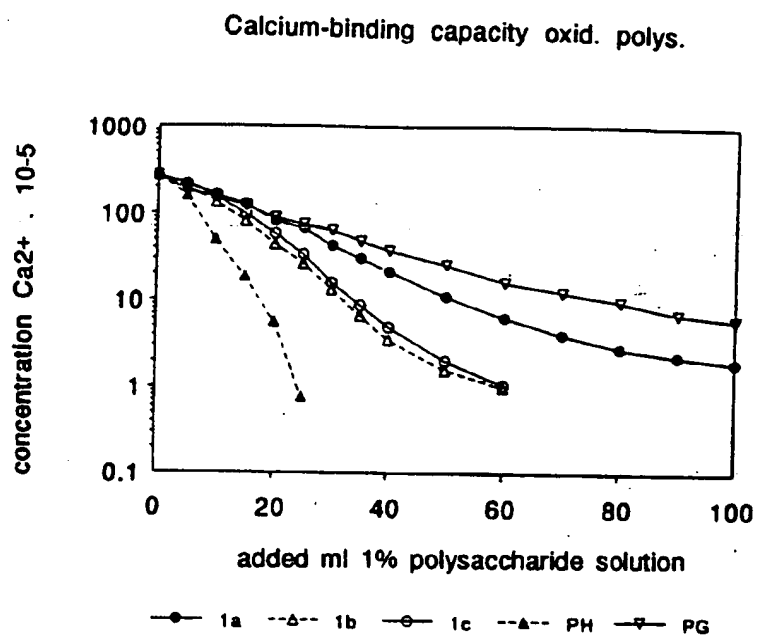
1/12

Figure 1 Calcium-binding capacity of the compounds according to Comparative Examples 1-5.



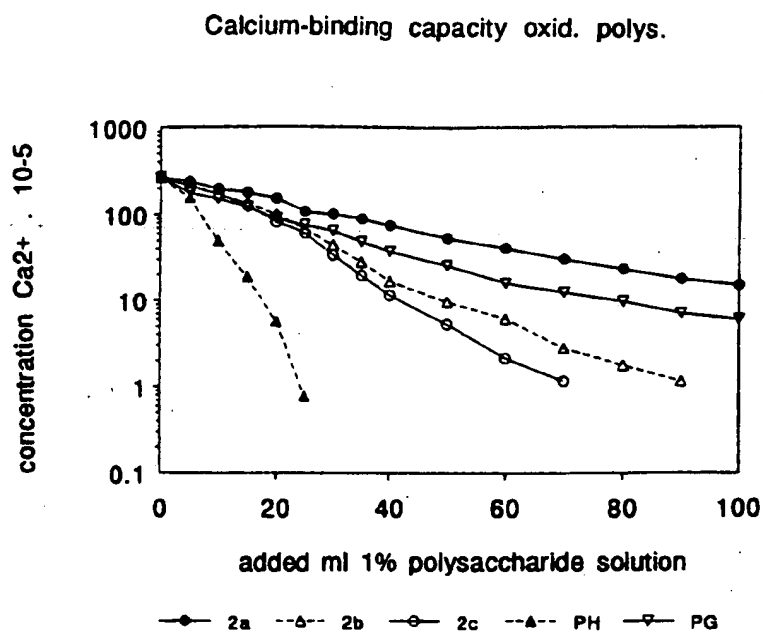
2/12

Figure 2 Calcium-binding capacity of the compounds 1a-1c
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



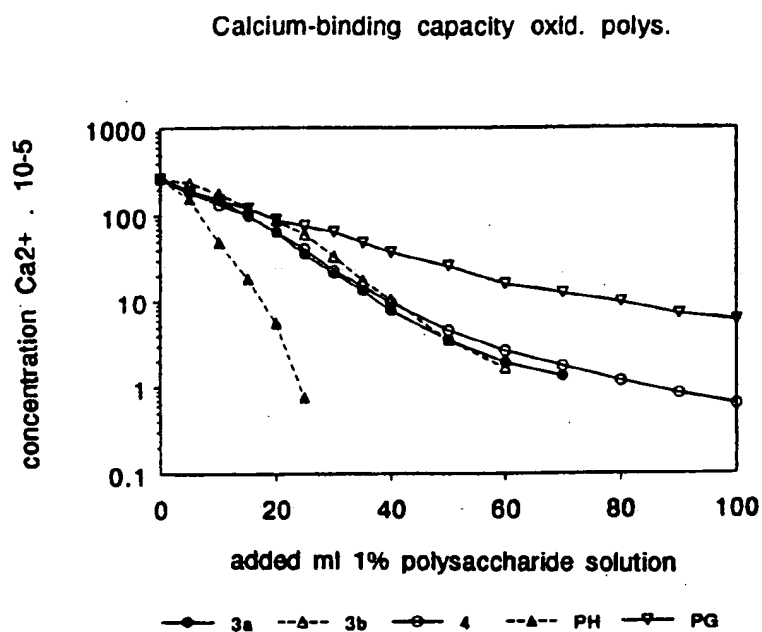
3/12

Figure 3 Calcium-binding capacity of the compounds 2a-2c
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



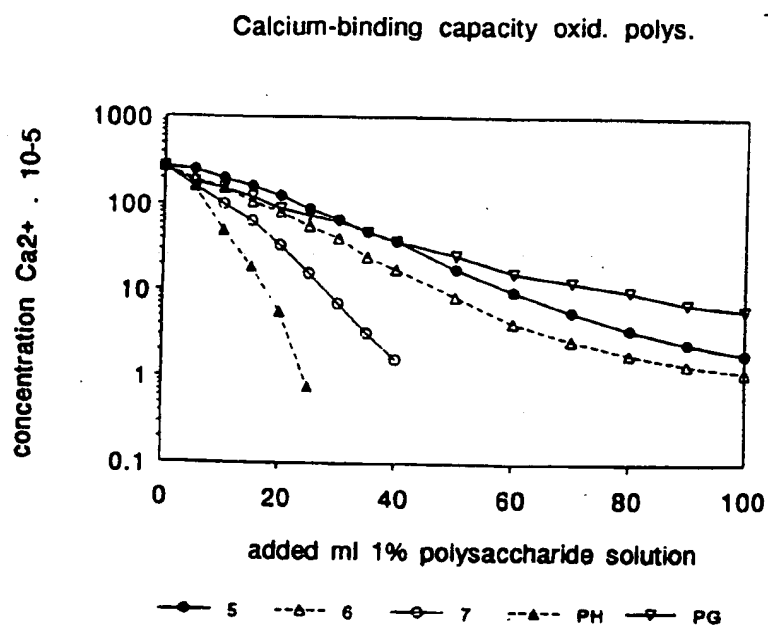
4/12

Figure 4 Calcium-binding capacity of the compounds 3a, 3b and 4 (PH = sodium tripolyphosphate, PG = polyglucuronic acid (Comparative Example 1)).



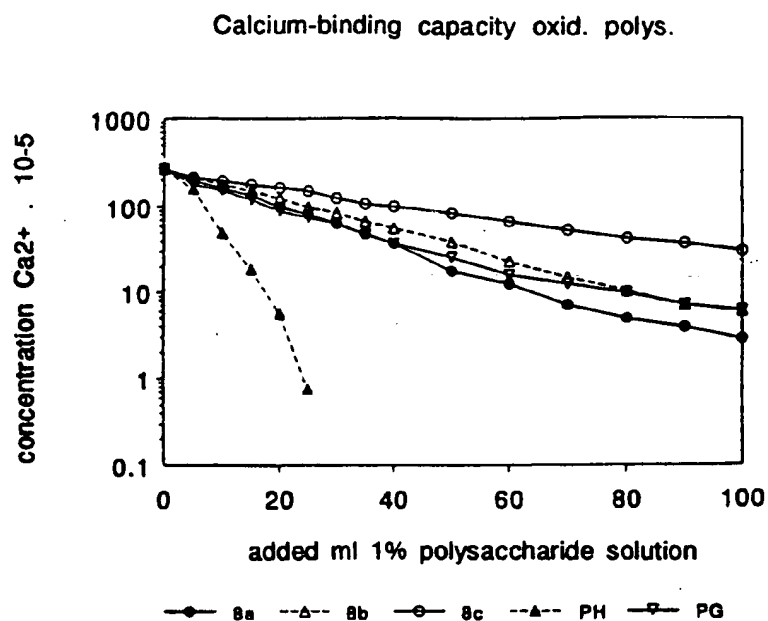
5/12

Figur 5 Calcium-binding capacity of the compounds 5, 6 and 7
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



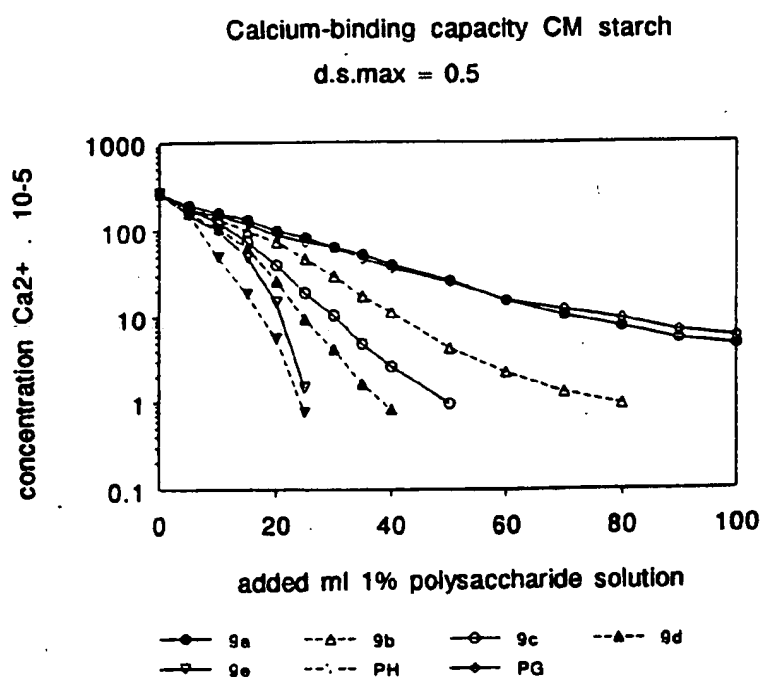
6/12

Figur 6 Calcium-binding capacity of the compounds 8a-8c
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



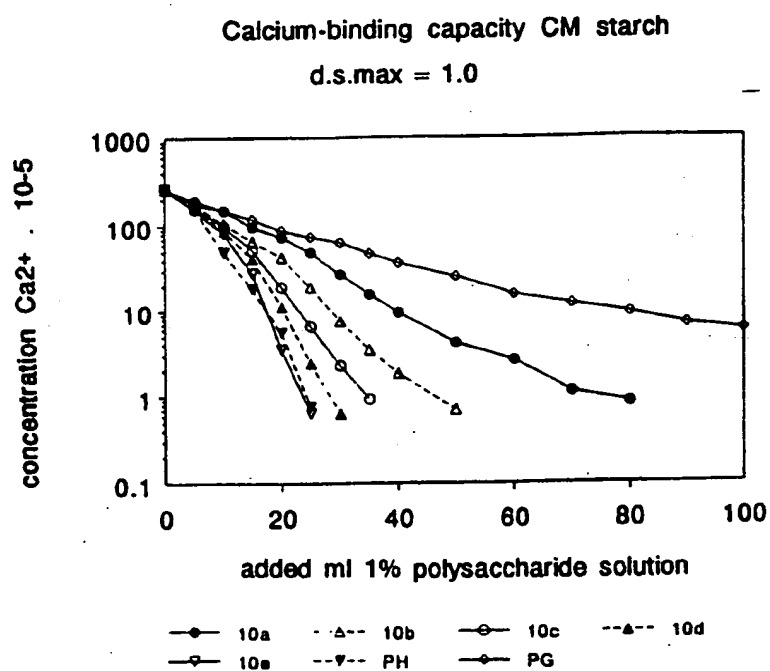
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Figure 7 Calcium-binding capacity of the compounds 9a-9e
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



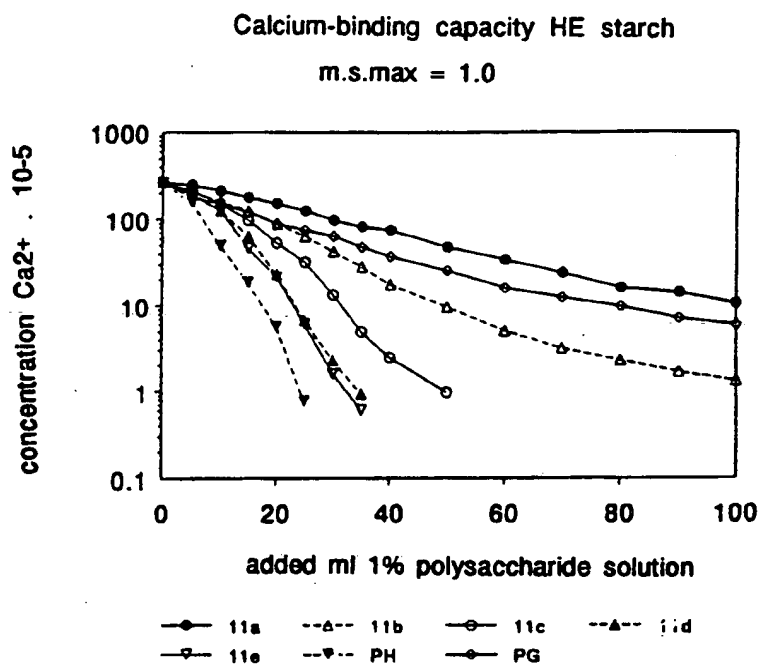
8/12

Figure 8 Calcium-binding capacity of the compounds 10a-10e
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



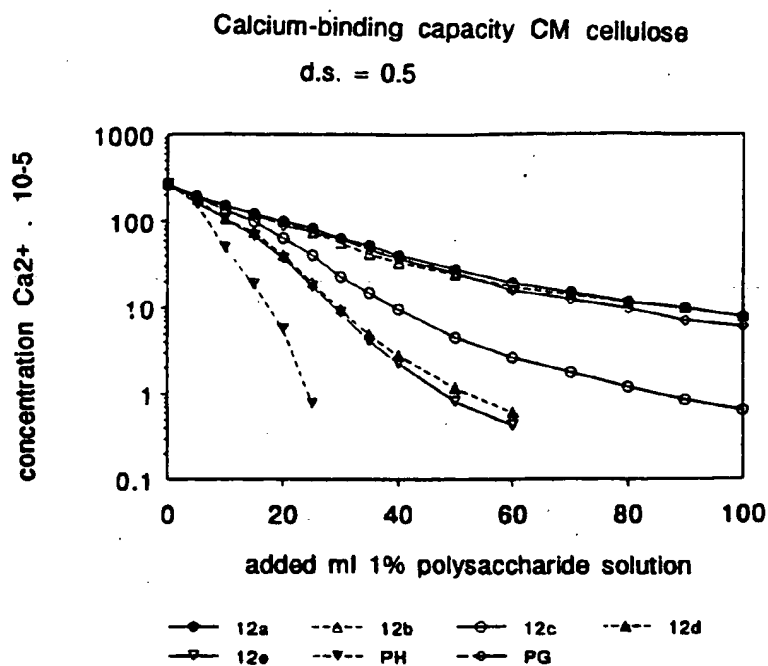
9/12

Figur 9 Calcium-binding capacity of the compounds 11a-11e
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



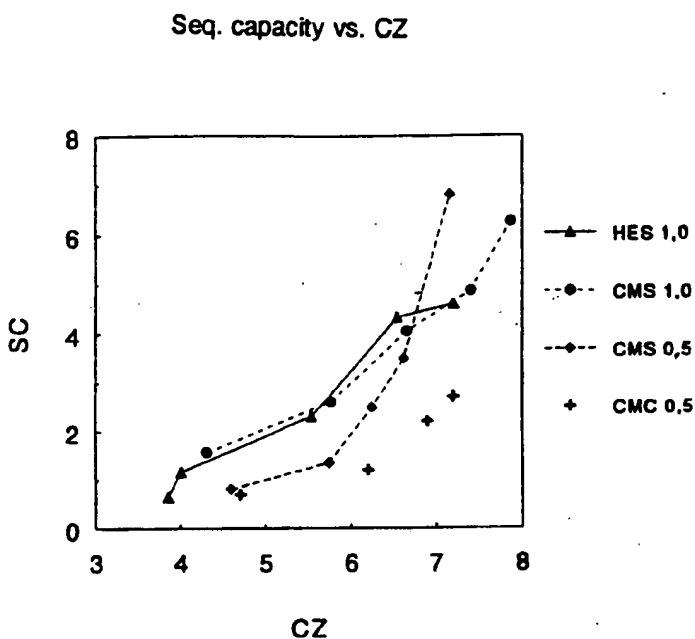
10/12

Figure 10 Calcium-binding capacity of the compounds 12a-12e
(PH = sodium tripolyphosphate, PG = polyglucuronic acid
(Comparative Example 1)).



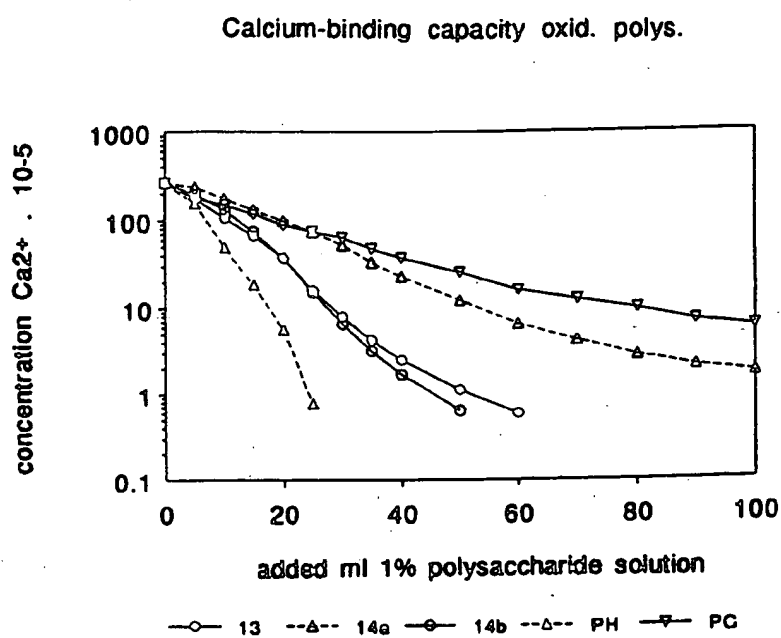
11/12

Figur 11 The sequestering capacity versus the carboxyl content of oxidized hydroxyethyl starch (HES), oxidized carboxymethyl starch (CMS) and oxidized carboxymethylcellulose (CMC), see Examples 9-12.



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Figure 12 Calcium-binding capacity of the compounds 13-14b
(PH = sodium tripolyphosphate, PG = polyglucuronic
acid (Comparative Example 1)).



INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 96/00218

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08B31/18 C08B11/20 C11D3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08B C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 9444 Derwent Publications Ltd., London, GB; AN 354775 XP002016639 & JP,A,06 279 504 (LION CORP) , 4 October 1994 see abstract	
A	EP,A,0 488 467 (SHELL) 3 June 1992	
A	WO,A,95 07303 (TNO) 16 March 1995 cited in the application	
A	GB,A,1 299 646 (LYCKEBY STARKELSEFORALDING) 13 December 1972 cited in the application	
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 October 1996

Date of mailing of the international search report

30. 10. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Lensen, H

INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 96/00218

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>RECEUIL DES TRAVAUX CHIMIQUES DES PAYS-BAS, vol. 113, no. 3, 1 March 1994, pages 165-166, XP000560836 A.E.J. DE NOOY ET AL.: "Highly selective tempo mediated oxidation of primary alcohol groups in polysaccharides." cited in the application</p> <p style="text-align: center;">---</p>	
A	<p>DATABASE WPI Week 7613 Derwent Publications Ltd., London, GB; AN 23409X XP002016641 & JP,A,51 017 387 (FUJI CHEMICAL IND KK) , 12 February 1976 cited in the application see abstract & CHEMICAL ABSTRACTS, vol. 84, no. 26, 28 June 1976 Columbus, Ohio, US; abstract no. 7617387, page 63; see abstract</p> <p style="text-align: center;">-----</p>	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 96/00218

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-488467	03-06-92	US-A- 5175360	29-12-92
		AU-B- 643339	11-11-93
		AU-A- 8806191	28-05-92
		CA-A- 2055804	27-05-92
		CN-A- 1061773	10-06-92
		DE-D- 69116826	14-03-96
		DE-T- 69116826	19-09-96
		ES-T- 2083516	16-04-96
		JP-A- 4283537	08-10-92

WO-A-9507303	16-03-95	NL-A- 9301549	03-04-95

GB-A-1299646	13-12-72	SE-B- 381877	22-12-75
		SE-B- 376427	26-05-75
		SE-B- 376243	12-05-75
		BE-A- 750581	03-11-70
		CA-A- 964216	11-03-75
		CH-A- 556808	13-12-74
		DE-A- 2023944	11-03-71
		FR-A- 2060503	18-06-71
		LU-A- 60925	16-07-70
		NL-A- 7007194	23-11-70
